Toward Silicon-Catenated Silole Polymers, Poly(1,1-silole)s: Syntheses and Structures of Oligo(1,1-silole)s (SYNTHETIC ORGANIC CHEMISTRY-Synthetic Design)

AUTHOR(S):

Yamaguchi, Shigehiro; Jin, Ren-Zhi; Tamao, Kohei

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Shigehiro Yamaguchi, Ren-Zhi Jin, and Kohei Tamao

A series of 1,1-difunctionalized siloles have been synthesized from 1,1-diaminosiloles, which have been prepared via the intramolecular reductive cyclization of diaminobis(phenylethynyl)silane. With the 1,1-difunctionalized siloles in hand, oligo(1,1-silole)s, silole oligomers catenated through silicons, have been synthesized as model compounds of poly(1,1-silole)s. UV absorption spectra of the oligosiloles have been determined, in which tersilole and quatersilole have unique absorption maxima around 280-290 nm.

Keywords: Silole / Poly(1,1-silole) / Oligo(1,1-silole) / σ*–π* Conjugation / Polysilane / Intramolecular reductive cyclization / UV absorption spectra

Poly(1,1-silole)s, silole (silacyclopentadiene) polymers catenated through the ring-silicons, constitute a new class of polysilanes with σ*–π* conjugation, as shown in Figure 1. In the silole ring itself, there is a significant low-lying LUMO energy level due to the σ*–π* conjugation arising from the interaction of the σ* orbital of the two exocyclic σ bonds on silicon with the π* orbital of the *cisoid*-butadiene moiety [1]. This type of orbital interaction would also take place in the polymeric system, as schematically shown in Figure 1. Thus, σ*–π* conjugation between the σ* orbital delocalized over the polysilane main chain and the π*-orbital localized on the *cisoid*-butadiene moiety in every silole ring would lower the LUMO level. Poly(1,1-silole)s are thus interesting target molecules to synthesize, while only a few silole dimers have been synthesized to date. Reported herein are our recent results toward the still veiled poly(1,1-silole)s.

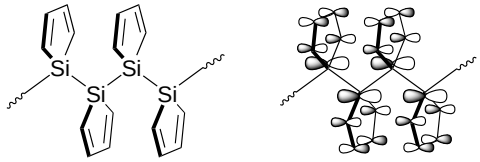


Figure 1. Schematic drawings of Poly(1,1-silole) and σ*–π* conjugation in the LUMO.

1. A New Synthetic Route to 1,1-Difunctionalized Siloles [2]

For the synthesis of poly(1,1-silole)s, 1,1-functionalized siloles, especially 1,1-dichlorosiloles, are an important class of compounds as starting materials. However, their synthetic methodologies have been rather limited. We have now developed a new general

SYNTHETIC ORGANIC CHEMISTRY –Synthetic Design–

Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π-conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfoniun and episelenonium ions.

Prof TAMAO, Kohei (D Eng)

Assoc Prof TOSHIMITSU, Akio (D Eng)

Instr KAWACHI, Atsushi (D Eng)

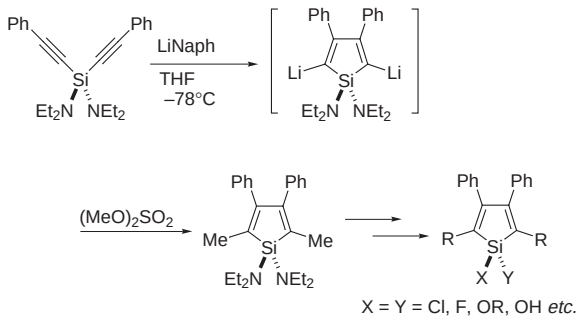
Instr YAMAGUCHI, Shigehiro (D Eng)

KATKEVICS, Martins (Guest Res Scholar); JIN, Ren-Zhi (Guest Scholar); ASAHARA, Masahiro (DC); TANAKA, Yoko (DC); AKIYAMA, Seiji (DC); ISHII, Hiroyuki (MC); TERADA, Masayoshi (MC); ITAMI, Yujiro (MC); ENDO, Tomonori (MC); MITSUDO, Koichi (UG); GOTO, Tomoyuki (UG); SAEKI, Tomoyuki (UG); SANO, Atsushi (UG)

synthetic route to 1,1-functionalized siloles using 1,1-diaminosiloles as key compounds.

Our method is based on the intramolecular reductive cyclization of bis(phenylethynyl)silanes, which we have recently developed [3]. Thus, bis(diethylamino)bis(phenylethynyl)silane was added dropwise into an excess amount of lithium naphthalenide (4 molar amount) at –78 °C to form 2,5-dilithio-1,1-diaminosilole cleanly. The dilithiosilole was successfully trapped with dimethyl sulfate to form 2,5-dimethyl-1,1-diaminosilole in good yield. A series of 1,1-difunctionalized siloles having alkoxy, Cl, and F functionalities were prepared by the conventional functional group transformation from 1,1-diaminosiloles (Scheme 1). The present methodology is also applicable to the synthesis of 1-monofunctionalized siloles.

Scheme 1

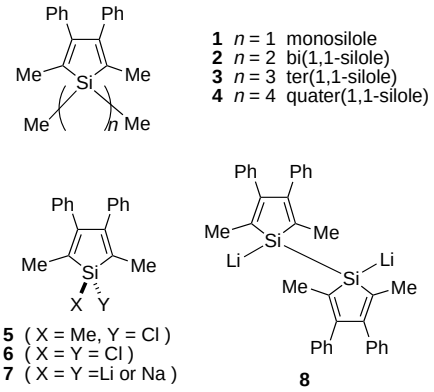


2. Oligo(1,1-silole)s as Models of Poly(1,1-silole)s [4]

With the silicon-chlorinated siloles **5** and **6** in hand, we have succeeded in the preparation of a series of oligo(1,1-silole)s from dimer **2** to tetramer **4** (Chart 1). Thus, silole trimer, tersilole **3**, has been obtained by the coupling of monochlorosilole **5** with silole dianion **7**, which was cleanly prepared from 1,1-dichlorosilole **6** with Li in THF. Quatersilole **4** has also been obtained by a similar coupling reaction. Thus, 1,1-dichlorosilole **6** was reduced with 3 molar amount of Na, resulting in the formation of a mixture of the bisilole dianion **8** and the silole dianion **7**. The mixture was treated with 1.5 molar amount of 1-chlorosilole to afford quatersilole **4** and tersilole **3** in 20% and 8% yields, respectively. These are the first examples of oligo(1,1-silole)s catenating more than three silole rings.

UV absorption data are summarized in Table 1, in which the data of the perphenyl- and permethyl-trisilanes and tetrasilanes are also given for comparison. The monosilole **1** has two absorption bands around 250 nm and 310 nm, assignable to the π–π* transitions of the

Chart 1



phenyl and silole moieties, respectively. In comparison with the monosilole **1**, the oligosiloles **2**-**4** show distinct spectra, where the absorption of the silole moieties is hidden by broad bands. Remarkably, tersilole **3** and quatersilole **4** have unique absorptions at around 280 and 290 nm, respectively. These absorption maxima are 50-60 nm longer than those of the permethyl oligosilanes. In comparison with the perphenyl counterparts, **3** has a 20 nm longer λ_{max} and **4** has a comparable λ_{max}. As mentioned previously, the unique absorptions of the oligo(1,1-silole)s would have arisen from the orbital interactions.

Table 1. UV Spectral Data for Oligo(1,1-silole)s[a]

compound	λ_{max} / nm	logε
monosilole **1**	307	3.22
bisilole **2**	255	4.42
tersilole **3**	279	4.60
quatersilole **4**	289	4.59
$Ph(Ph_2Si)_3Ph$[b]	255	4.51
$Ph(Ph_2Si)_4Ph$[c]	288	4.36
$Me(Me_2Si)_3Me$[d]	216	3.96
$Me(Me_2Si)_4Me$[d]	235	4.17

[a] In chloroform. [b] Gilman H, Atwell W. H, Sen P. K, and Smith C. L, *J. Organomet. Chem.*, **4**, 163 (1964). [c] Gilman H, and Atwell W. H, *J. Organomet. Chem.*, **4**, 176 (1964). [d] Gilman H, Atwell W. H, and Schwebke G. L, *J. Organomet. Chem.*, **2**, 369 (1964).

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